Remarks

Claims 1-20 are pending. Claims 10 and 13-20 are withdrawn.

No claim amendments have been made.

The rejection of claims 1, 2, 4, and 6-8 as being rejected under 35 USC 102(a) as being anticipated by Huang et al, and claims 3, 5, 9, 11 and 12 under USC 103(a) as being unpatentable variously over Huang in view of Hsu or Yu, is respectfully traversed.

Applicant now wishes to establish their invention of the subject matter prior to the effective date of the reference (*i.e.* Huang scientific publication date of January 28, 2004).

A declaration under 37 CFR 1.131 signed by all the inventors:

All the inventors have signed a declaration (see **Exhibit 1**) attesting that to their knowledge and belief a copy of their invention disclosure (see **Exhibit 2**) was submitted to their University's Technology Transfer Office on December 8, 2003. Indeed, on page 5 of exhibit 2 Drs. Iyer and Liu actually signed the disclosures on December 2, 2003 and December 5, 2003, respectively. This suggests that the work (manuscript attached to the invention disclosure) was completed as early as December 2, 2003, if not earlier, which is prior to the Huang publication date of January 28, 2004. Accordingly, without having access to the Huang reference, the basis for the above 102 and 103(a) rejections are improper and the rejection should be withdrawn.

Some information in **Exhibit 2** relating to dates of conception has been redacted. It should also be noted that they the inventors attested that their work was performed in the US.

Discussion of Invention Disclosure (**Exhibit 2**)

As should be evident to a person of skill in the art, part of the invention disclosure (pages 6-19) are in the form of a draft manuscript to be submitted to a peer reviewed journal. It is then evident that the disclosure describes experiments actually performed (*i.e.* a reduction to practice), and a discussion of them.

For instance, the abstract essentially discloses a reduction to practice of the claims prior to the prior art date of Huang, to wit:

> "We report the synthesis of a cationic conjugated co-polymer, poly ([9, 9-bis (6 '. (N, N, N-trimethylammonium) hexyliodide)-fluorene-2, 7 –diyl]-alt-[2,5 –bis (p-phenylene)-1,3.4-oxadiazole]},. (poly l).and the introduction of poly1 as an electron-transport layer (ETL) in polymer light emitting diodes (PLEDs). Multilayer PLEDs are fabricated using semiconducting polymers cast from solution in an organic solvent as an emissive layer and the water-soluble (or methanol-soluble) poly l, as an ETL in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. The results demonstrate that devices with poly l have significantly lower turn-on voltages, higher brightness and improved luminous efficiency."

More particularly, the following table shows evidence of Applicant's claim 1 limitations in the invention disclosure prior to the Huang reference date, to wit:

Applicant's claim 1 limitations	Disclosed by Invention disclosure sent on December 8, 2003
"...providing a first solution comprising a first material that is a water-soluble cationic conjugated polymer and a first solvent; .." and "...depositing a first layer of one of said first and second solutions onto a substrate;..."	See page 12 (referring to compound 'poly 1'; see also page 8 of Invention disclosure, paragraph 2, line 8 (where poly 1 is used to fabricate a PLED).
"...providing a second solution comprising a second material and a	See page 12 (where semiconducting polymers are cast from solution in an

second solvent; ..” and “depositing a second layer of the other of said first and second solutions onto the first layer; wherein the material deposited in the first layer does not dissolve in the solvent deposited in the second layer”	organic solvent to fabricate a PLED with poly 1). See also page 8 of Invention disclosure, paragraph 2, line 7 (i.e. semiconducting polymer in an organic solvent).
“...	See also Figures 1 and 2 on pages 18 and 19, respectively showing the successful fabrication of a device made using the claimed method.

Thus, the entire evidence, as submitted, proves that Applicant had reduced to practice the claimed invention in the US prior to the publication date of Huang (January 28, 2004). Accordingly, the Huang reference should not be available as prior art under both 102(a) and 103 (a), and these rejections should be withdrawn.

In view of the foregoing, applicant urges the examiner to reconsider the obviousness rejections.

The Commissioner is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 50-3881.

Dated: January 3, 2011

Respectfully submitted,

By________________

Richard Y.M. Tun, Ph.D.
Registration No.: 56,594
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555 West Fifth Street, 31st Floor
Los Angeles, California 90013

(213) 533-4175 (Telephone)
(213) 533-4174 (Fax)

EXHIBIT # 1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Guillermo C. Bazan	)
		)
Serial No.:	10,595,179	) Examiner: R. S. Walters
		)
Filed:	August 21, 2006	) Art Unit: 1711
		)
For:	METHODS AND DEVICES COMPRISING SOLUBLE CONJUGATED POLYMERS	)Confirmation no. 3968
		)
Atty. Dkt. No.:	1279-454	)
		)

BERLINER & ASSOCIATES
555 West Fifth Street, 31st Floor
Los Angeles, California 90013

Mail Stop: Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF INVENTORS UNDER 37 CFR 1.131

We, the below named inventors, hereby declare that:

1) We are inventors of and are knowledgeable about the subject matter disclosed in the application entitled METHODS AND DEVICES COMPRISING SOLUBLE CONJUGATED POLYMERS, the specification of which was filed on August 21, 2006 and has been assigned Serial No. 10,595,179.

2) Attached as exhibit #2 is a copy of an invention disclosure submitted to our University's Office of Technology on December 8, 2003.

3) The work described in the invention disclosure took place in the United States.

We hereby declare that all statements made herein of my knowledge are true and

that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signature of Inventors

1) **Alan J. Heeger**

Inventor's signature: Alan J Heeger　　Date: 12/20/2010

2) **Guillermo C. Bazan**

Inventor's signature: ____________________　　Date: __________

3) **Xiong Gong**

Inventor's signature: ____________________　　Date: __________

4) **Wanli Ma**

Inventor's signature: ____________________　　Date: __________

5) **Parameswar K. Iyer**

Inventor's signature: ____________________　　Date: __________

6) **Bin Liu**

Inventor's signature: ____________________　　Date: __________

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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		)
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Signature of Inventors

1) **Alan J. Heeger**

Inventor's signature:____________________ Date: __________

2) **Guillermo C. Bazan**

Inventor's signature: ____________________ Date: 12/22/10

3) **Xiong Gong**

Inventor's signature:____________________ Date: __________

4) **Wanli Ma**

Inventor's signature:____________________ Date: __________

5) **Parameswar K. Iyer**

Inventor's signature:____________________ Date: __________

6) **Bin Liu**

Inventor's signature:____________________ Date: __________

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Guillermo C. Bazan)
)
Serial No.: 10,595,179) Examiner: R. S. Walters
)
Filed: August 21, 2006) Art Unit: 1711
)
For: METHODS AND DEVICES COMPRISING) Confirmation no. 3968
SOLUBLE CONJUGATED POLYMERS)
)
Atty. Dkt. No.:1279-454)
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Inventor's signature:________________ Date: ________

2) **Guillermo C. Bazan**

Inventor's signature:________________ Date: ________

3) **Xiong Gong**

Inventor's signature:________________ Date: 12/17/10

4) **Wanli Ma**

Inventor's signature:________________ Date: ________

5) **Parameswar K. Iyer**

Inventor's signature:________________ Date: ________

6) **Bin Liu**

Inventor's signature:________________ Date: ________

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Signature of Inventors

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Inventor's signature:______________ Date: ________

2) **Guillermo C. Bazan**

Inventor's signature:______________ Date: ________

3) **Xiong Gong**

Inventor's signature:______________ Date: ________

4) **Wanli Ma**

Inventor's signature: Date: 2010-12-27

5) **Parameswar K. Iyer**

Inventor's signature:______________ Date: ________

6) **Bin Liu**

Inventor's signature:______________ Date: ________

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Inventor's signature:________________ Date: ________

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Inventor's signature:________________ Date: ________

3) **Xiong Gong**

Inventor's signature:________________ Date: ________

4) **Wanli Ma**

Inventor's signature:________________ Date: ________

5) **Parameswar K. Iyer**

Inventor's signature: Iyer Date: 12/22/10

6) **Bin Liu**

Inventor's signature:________________ Date: ________

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Guillermo C. Bazan	)
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Serial No.:	10,595,179	) Examiner: R. S. Walters
		)
Filed:	August 21, 2006	) Art Unit: 1711
		)
For:	METHODS AND DEVICES COMPRISING SOLUBLE CONJUGATED POLYMERS	) Confirmation no. 3968
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Signature of Inventors

1) **Alan J. Heeger**

Inventor's signature:________________ Date: ________

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Inventor's signature:________________ Date: ________

3) **Xiong Gong**

Inventor's signature:________________ Date: ________

4) **Wanli Ma**

Inventor's signature:________________ Date: ________

5) **Parameswar K. Iyer**

Inventor's signature:________________ Date: ________

6) **Bin Liu**

Inventor's signature:________________ Date: Dec 15, 2010

EXHIBIT # 2

Office of Research
3227 Cheadle Hall
University of California
Santa Barbara, CA 93106-2050

UCSB

Fax-confidential

To:	Linda Stevenson	**From:**	Tish Ramos
Fax:	510.587-6090	**Pages:**	18 pages to follow cover sheet
Phone:		**Date:**	December 8, 2003
Re:	Disclosure and Record of Invention Form	**Fax:**	X2611 **Phone:** 893.7881
		email:	ramos@omni.ucsb.edu

☐ Urgent ☐ For Review ☐ Please Comment ☐ Please Reply ☐ Please Recycle

Linda-

Per the request of Sherylle Mills Englander, Director Sponsored Projects, she would prefer that Oren Liven review this disclosure. This invention disclosure is from Guillermo Bazan, Alan Heeger, Parameswar Iyer, Bin Liu, Wanli Ma, Xiong Gong and Daniel Moses titled "Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light Emitting Diodes." I'll be mailing the original today.

☺

Tish

University of California | Office of Technology Transfer

DISCLOSURE AND RECORD OF INVENTION FORM

Note: When completed, the Disclosure and Record of Invention Form is an important legal document. Care should be taken in its preparation. Please refer to accompanying instructions. If you desire assistance, call the Office of Technology Transfer (University Patent Office) at (510) 748-6600. Information contained in this document is maintained in confidence by the University Patent Office and normally will not be released to others except with attorney-client privilege; to research sponsors as required by contract, or under appropriate secrecy agreements, until a patent application is filed, the information is published, a determination not to file a patent application is made, or as may be required by law. The information contained should not be disclosed to others outside the University, except as described in section 9, without the approval of the University Office of Technology Transfer. It is the practice of the University Office of Technology Transfer to send your Record of Invention to other University employees for peer review.

b. Short descriptive title of the invention.

Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light Emitting Diodes

2. A. Briefly summarize the invention here. Include the novel features and advantages.

A method is provided for the design of conjugated polymers suitable for improving the efficiency of polymer light emitting diodes. Water solubility provides for these materials to be spin cast on top of standard organic solvent-soluble conjugated polymers with minimum disruption of the underlying layer. There may be two components to this invention. First, general design guidelines for polymers that are soluble in polar solvents and that may serve as either an electron- or a hole-transport layer. Second, the use of these polymers in a range of organic optoelectronic devices.

B. Detailed description of the invention using additional sheets as necessary and attach as appendix.

See attached document.

3. List the funding source(s) for the project under which this invention was made. If applicable, identify by contract or grant number and name the Principal Investigator/Supervisor of each.

Funding Source/Sponsor	Contract or Grant Number	Principal Investigator/Supervisor
DuPont Displays	SB030014	Guillermo C. Bazan
UC-SMART	01-10110	Guillermo C. Bazan
Mitsubishi Chemical Corporation	Contract number SB010061	Alan J. Heeger

4. For any Inventor named (item 13) who is not employed full-time by the University of California, please identify other employers (e.g., Veterans Administration, Howard Hughes Medical Institute, USDA), the percent of salary time funded by such other employer, and the nature of the other employment (such as research, teaching or clinical duties).

5. When did you first conceive this invention?

[redacted] [redacted]

6 What is the date of the first written record (notebook, letter, proposal, drawing, etc.) of this invention? Identify the document, page numbers involved, and location of the document.

[redacted] Information is in [redacted] (Iyer's notebook # 2, located in Bazan Group's lab/office. Chemistry 2614)

6. When did you first successfully test this invention?

The polymer was successfully synthesized on [redacted]
Devices were first tested on [redacted]

8. If you have disclosed this invention to non-UC personnel (including research sponsor) then indicate when, under what circumstances, and to whom.

a. [redacted]

[redacted]

c. [redacted].

c. by actual use, demonstration, or posters

7. Have you submitted or do you plan to submit a report, abstract, paper or thesis relating to this invention for publication, for presentation at a conference, or to a research sponsor?

Yes, we have prepared a manuscript, which we would like to submit to Advanced Materials as soon as possible.

If yes, give details, including the actual or planned date of submission. If a manuscript has been accepted, give the anticipated publication date. Append a copy of the latest draft manuscript available. (See instructions for the effect of publication prior to the filing of a patent application.)

8. Identify any references, patent applications, or other publications of which you are aware and which you believe to be pertinent to this invention. Please attach a copy of each of these references, if available.

See attached document.

11. If any proprietary material (e.g., cell line, antibody, plasmid, computer software, or chemical compound) obtained from outside your laboratory was used to develop this invention under a restrictive written or oral transfer agreement (other than a normal purchasing agreement), please attach a copy or summary of that agreement.

12. List companies you believe might be interested in using, developing or marketing this invention.

Mitsubishi Chemical, DuPont Displays

13. Signatures, Names, and Addresses of Inventors

Signature / Date	Signature / Date
Print Name: Guillermo C. Bazan	Print Name: Alan J. Heeger
Dept/ORU: Institute for Polymer and Organic Solids, Departments of Chemistry and Materials	Dept/ORU: Institute for Polymer and Organic Solids, Department of Materials
Rm & Bldg: Chemistry 2120	Rm & Bldg: Chemistry 2120
Campus (Address if non-UC): UCSB	Campus (Address if non-UC): UCSB
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Note: if there are more inventors please provide signatures, names and addresses on an additional sheet of paper.

Signatures, Names, and Addresses of Inventors

Signature Date

Print Name

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Institute for Polymer and Organic Solids
Departments of Chemistry and Materials

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Campus (Address if non-UC)
UCSB

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Telephone

Facsimile

Email

Signature Date

Print Name

Dept/ORU

Rm & Bldg

Campus (Address if non-UC)

City/State/Zip

Telephone

Facsimile

Email

Note: if there are more inventors please provide signatures, names and addresses on an additional sheet of paper.

14. Technically Qualified Witnesses (Two Required) - invention disclosed to and understood by:

a) [signature] 12/05/03
Signature Date

H. Benmansour
Print Name
Dr. Hadjar Benmansur

b) [signature] 12-5-03
Signature Date

David A Banach
Print Name
Mr. David Banach

Submit this form with ORIGINAL SIGNATURES directly to:

Director - Office of Technology Transfer
Office of the President
University of California
1320 Harbor Bay Parkway, Suite 150
Alameda, CA 94502

If you do not receive an acknowledgment within 30 days, please call the University Office of Technology Transfer at (510) 748-6600.

NOTE: DISTRIBUTION OF COPIES OF A COMPLETED FORM TO THIRD PARTIES IS EXPRESSLY PROHIBITED, AS PROPRIETARY UNIVERSITY INFORMATION IS CONTAINED IN ANY COMPLETED FORM.

Retention: 7 years after last patent expires or 10 years after the date of the last action, whichever is later.

Signature

Date
12/02/03

Print Name
Parameswar K. Iyer

Dept/ORU
Institute for Polymer and Organic Solids
Departments of Chemistry and Materials

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Water/Methanol Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light Emitting Diodes

Parameswar K. Iyer, Wanli Ma, Xiong Gong, Bin Liu, Guillermo C. Bazan[1]*, Daniel Moses* and Alan J. Heeger*[2]

Institute for Polymers and Organic Solids
and
Mitsubishi Chemical Center for Advanced Materials
University of California at Santa Barbara,
Santa Barbara, CA 93106

* Corresponding authors E-mails: bazan@chem.ucsb.edu, moses@ipos.ucsb.edu, ajh@physics.ucsb.edu, Fax: (805)-893-4755,
[1] Departments of Chemistry and Materials, UC Santa Barbara, Santa Barbara, CA 93106
[2] Departments of Physics and Materials, UC Santa Barbara, Santa Barbara, CA 93106

Abstract

We report the synthesis of a cationic conjugated co-polymer, poly{[9,9-bis(6'-(N,N,N-trimethylammonium)hexyliodide)-fluorene-2,7-diyl]-alt-[2,5-bis(p-phenylene)-1,3,4-oxadiazole]}, (poly1), and the introduction of poly1, as an electron-transport layer (ETL) in polymer light emitting diodes (PLEDs). Multilayer PLEDs are fabricated using semiconducting polymers cast from solution in an organic solvent as an emissive layer and the water-soluble (or methanol-soluble) poly1, as an ETL in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. The results demonstrate that devices with poly1 have significantly lower turn-on voltages, higher brightness and improved luminous efficiency.

Keywords:

Water-soluble conjugated co-polymer, electron-transporting layer, multi-layer polymeric light-emitting diodes, electroluminescence.

The principal criteria for a polymer based electron transport layer (ETL) for use in polymer light-emitting diodes (PLEDs) are the following: (1) the lowest unoccupied molecular orbital (LUMO) of the ETL must be at an energy close to, or even within the π^*-band of the emissive semiconducting polymer; and (2) the solvent used for casting the electron injection material must not dissolve the underlying emissive polymer. Although a few attempts to satisfy these criteria have been reported, [1, 2] none has succeeded in avoiding interfacial mixing in multi-layer PLEDs.

In this contribution, we report the synthesis of the cationic conjugated alternating copolymer, poly {[9,9-bis(6'-(N,N,N-trimethylammonium)hexyliodide)-fluorene-2,7-diyl]-alt-[2,5-bis(p-phenylene)-1,3,4-oxadiazole]}, (poly**1**), comprising fluorene and phenylene-oxadiazole-phenylene alternating along the main chain, by the palladium catalyzed Suzuki coupling reaction (Scheme 1). Multi-layer PLEDs are fabricated using a semiconducting polymer (red, green or blue emitting) (Scheme 2), cast from solution in an organic solvent, as an emissive layer and the water-soluble (or methanol-soluble) poly**1** as an ETL in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. To our knowledge, there are no previous reports of the fabrication of multi-layer PLEDs using a water-soluble conjugated polymer as an ETL to solve the interfacial mixing problem. The results demonstrate that devices with the ETL have significantly lower turn-on voltages, higher brightness and improved luminous efficiencies.

<Scheme 1>

<Scheme 2>

The synthesis of poly**1** is shown in Scheme 1. Monomers 2[3] (0.440 gm, 0.654 mmol) and 3[4] (0.247 gm, 0.654 mmol) were dissolved in 20 mL toluene. Sodium carbonate (0.694 gm, 6.54 mmol) and $Pd(PPh_3)_4$ (0.037 gm, 0.0327 mmol) were

added to the reaction mixture, followed by 5 mL water. The reaction was degassed and refluxed for 48 hours under an argon atmosphere. Isolation, followed by triple precipitation into acetone gave poly{[9,9-bis(6'-(N,N-dimethylamino)hexyl)-fluorene-2,7-diyl]-alt-[2,5-bis(p-phenylene)-1,3,4-oxadiazole]} (poly4, 0.231 gm, 55 %). Addition of MeI to a solution of poly4 results in the formation of a precipitate. Addition of water renders the reaction mixture homogenous. After 48 hours poly1 can be isolated and purified by repeated precipitation into acetone in approximately 86 % yield.

Figure 1 compares the current density vs. voltage and brightness vs. voltage characteristics of devices made using PFO with and without poly1. The PFO/ETL devices turn on at ~ 3V (the turn-on voltage is defined as the voltage at a brightness of 0.1 cd/m^2), whereas the turn-on voltage is at ~5V for the PFO devices without the ETL. [5] At 6V, the luminance (L) obtained from the PFO/ETL devices is L = 3450 cd/m^2, compared to L = 30 cd/m^2 for devices without the ETL. Similar improvements were observed from devices made with green and red emitting conjugated polymers. For MEH-PPV/ETL devices, L = 5600 cd/m^2 at 5V, compared to L= 3550 cd/m^2 for similar devices fabricated without the ETL. Therefore, the addition of the ETL results in lower turn-on voltage and higher brightness. The dramatic improvement in brightness and the reduced turn-on voltage result from improved electron injection (there is a good match of the LUMO of the ETL to the π*-band of the emissive polymer) and from the hole blocking capability of the ETL (LUMO energy at -6.24 eV relative to the vacuum).

<Figure 1>

PLEDs, the device efficiency is reduced by cathode quenching since the recombination zone is typically located near the cathode. [6] The addition of the ETL

moves the recombination zone away from the cathode and thereby eliminates cathode quenching. In addition, the ETL serves to block the diffusion of metal atoms, such as barium and calcium, and thereby prevents the generation of quenching centers [6] during the cathode deposition process. The luminous efficiency (LE in cd/A) vs. current density (J in mA/cm^2) for devices with and without the ETL are shown in Figure 2a, 2b and 2c. As shown in Figure 2, devices with ETL have higher luminous efficiency, higher power efficiency, and correspondingly higher brightness at a given voltage.

<Figure 2>

The improvements in LE and PE can be understood in greater detail by comparing the LUMO energy levels of the emissive polymers with that of poly1 and the work-function of barium (see Scheme 3). The energy barrier between the LUMO of PFO and the work function of barium is ~ 0.6 eV. Thus, by adding the poly1 layer, electron injection is enhanced. For PFO-BT and MEH-PPV, there is no energy barrier for electron injection. However, the hole-blocking feature of poly1 leads to better balanced electron and hole currents. In addition, the enhanced electron injection can also facilitate hole injection. [7] Therefore, the larger and more nearly balanced electron and hole currents lead to higher luminous efficiencies in the devices with the ETL.

<Scheme 3>

Interfacialergetics are known to play an important role in the emission characteristics of organic LEDs. [8, 9] By adding the ETL between the cathode and the emissive polymer, the contacts at both interfaces are improved. Atomic force microscope (AFM) images show that the surface roughness of the ETL is larger than that of the emissive polymer. As a result, more effective electron injection is achieved

simply because of the increased contact area between ETL and cathode.

In conclusion, the watersoluble (and methanol soluble) conjugated co-polymer poly1, was designed, synthesized and then introduced as the ETL in multi-layer PLEDs. By casting the ETL from solution in methanol and the emissive layer from an organic solvent solution, interfacial mixing is avoided. Using blue, green or red emitting semiconducting polymers as the emissive layer and poly1 as the ETL, significant improvements in performance have been demonstrated. More importantly, our results indicate that high-performance multi-layer PLEDs can be fabricated by processing all the layers from solution.

Experimental

Characterization of polymer 3: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.29 (m, 4H), 7.87 (m, 6H), 7.68 (m, 4H), 2.14 (m, 20H), 1.30 (m, 4H), 1.13 (m, 8H), 0.77 (m, 4H). ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 164.76, 152.07, 144.97, 140.91, 139.12, 127.95, 127.62, 126.54, 121.60, 120.67, 59.91, 55.64, 45.57, 40.57, 30.11, 27.70, 27.31, 24.05. Gel permeation chromatography (GPC) analysis shows a molecular weight of Mn = 19300 g/mol and a polydispersity of 1.04.

Characterization of polymer 4: ^{1}H NMR (400 MHz, DMSO, ppm): δ 8.30 (m, 4H), 8.07 (m, 6H), 7.88 (m, 4H) 3.13 (m, 4H) 2.94 (m, 22H), 1.43 (m, 4H), 1.06 (m, 8H), 0.61 (m, 4H). ^{13}C NMR (125MHz, DMSO, ppm): δ 168.94, 151.58, 149.42, 143.62, 137.91, 127.65, 127.62, 126.58, 122.15, 120.98, 65.13, 55.28, 52.05, 42.94, 30.74, 28.710, 25.38, 21.88.

Poly(9,9-dihexyl-fluorene-co-benzothiadiazole) (PFO-BT) was synthesized using the Suzuki coupling reaction. [10, 11] Poly(9,9-dioctyfluorenyl-2,7-diyl) (PFO) and poly[2-methoxy-5-(2-ethyl-hexyloxy) -1,4-phenylene vinylene] (MEH-PPV) were

purchased from American Dye Source, Inc. (Canada). The molecular structures of PFO, PFO-BT, and MEH-PPV are shown in Scheme 2. The HOMO (highest occupied molecular orbital) and LUMO energy levels of PFO, PFO-BT, MEH-PPV and poly1 are shown in Scheme 3. The work functions of poly(3,4-ethylene dioxythiophene): poly(styrene sulfonic acid) (PEDOT:PSS) and barium are also shown for comparison in Scheme 3.

For device fabrication, we utilized PEDOTPSS on indium tin oxide (ITO) as the hole-injecting bilayer electrode. PLEDS were fabricated with and without the ETL layer in the following device structures: (ITO)/PEDOT:PSS/Emissive polymer/Ba/Al and (ITO)/PEDOT:PSS/Emissive Polymer/ETL/Ba/Al. Details of device fabrication and testing have been reported elsewhere; all fabrication steps were carried out inside a controlled atmosphere dry box under nitrogen atmosphere. [12, 13] The ETL was deposited on top of the emissive layer by spin-casting from solution in methanol (0.6% wt.-%) to form a poly**1** layer with thickness of approximately 30 nm and then annealed at 90°C for 2 hours to remove residual solvent. Hydrophilic methanol was used as the solvent (rather than water) to achieve better inter-layer wetting while maintaining well-defined multi-layers. Throughout this report, we will use the term "emissive polymer/ETL" to designate devices with the ETL.

Acknowledgement

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References

[1] M. Hwang, M. Hua, S. Chen, *Polymer.* **1999**, *40*, 3233.

[2] Y. Yang, Q. Pei, *J. Appl. Phys.* **1995**, *77*, 4807.

[3] a) M. Stork, B. S. Gaylord, A. J. Heeger, G. C. Bazan, *Adv. Mater.* **2002**, 14, 361. b) S. Wang, G. C. Bazan, *Adv. Mater.* **2003**, *15*, 1425.

[4] X. Zhan, Y. Liu, X. Wu, S. Wang, D. Zhu, *Macromolecules.* **2002**, *35*, 2529.

[5] M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737.

[6] V. Choong, Y. Park, Y. Gao, T. Wehrmeister, K. Müllen, B. R. Hsieh, C. W. Tang, *Appl. Phys. Lett.* **1996**, *69*, 1492.

[7] K. Murata, S. Cinà, N. C. Greenham, *Appl. Phys. Lett.* **2001**, *79*, 1193.

[8] J. Cui, Q. Huang, J. G. C. Veinot, H. Yan, T. J. Marks, *Adv. Mater.*, **2002**, *14*, 565.

[9] N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes, *Nature*. **1993**, *365*, 628.

[10] J. Huang, Y. Niu, W. Yang, Y. Mo, M. Yuan, Y. Cao, *Macromolecules*. **2002**, *35*, 6080.

[11] P. Herguth, X. Jiang, M. S. Liu, A. K.-Y. Jen, *Macromolecules*. **2002**, *35*, 6094.

[12] X. Gong, J. C. Ostrowski, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Funct. Mater.* **2003**, *13*, 439.

[13] X. Gong, J. C. Ostrowski, M.R. Robinson, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2002**, *14*, 581.

Figures and Schemes captions:

Scheme 1. Synthesis of poly**1** and poly**4**.

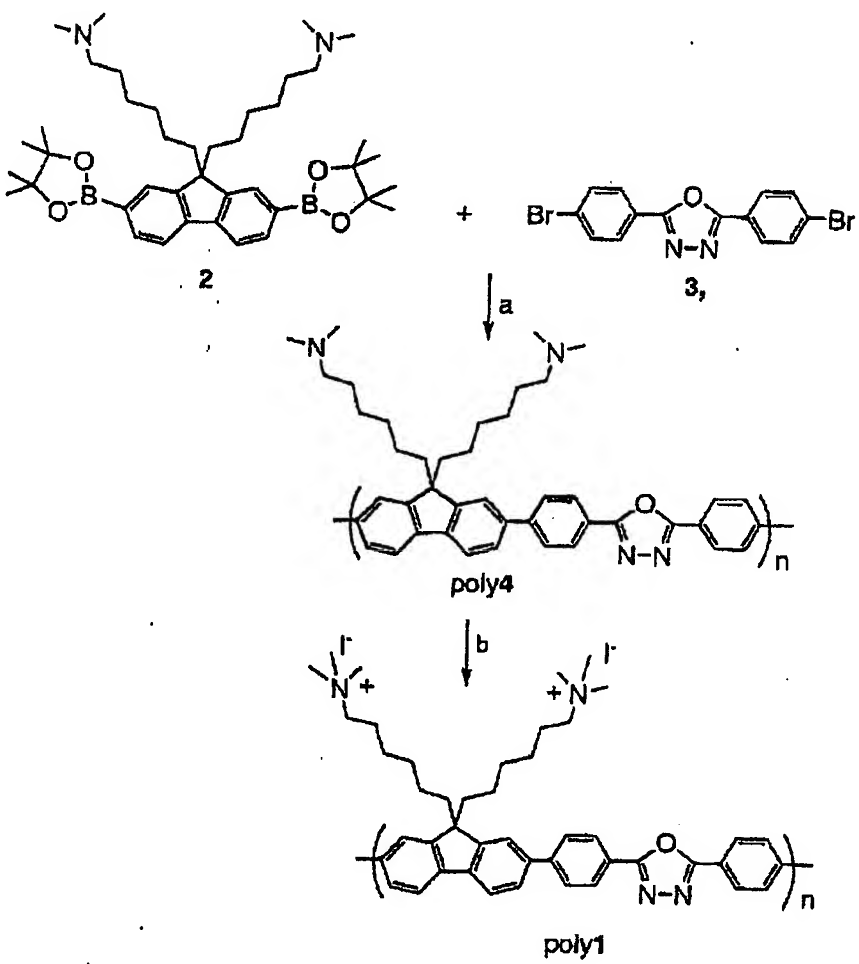
Scheme 2. Molecular structures of PFO, PFO-BT, and MEH-PPV.

Scheme 3. The HOMO and LUMO energy levels of PFO, PFO-BT, MEH-PPV and poly**1** compared to the work function of Ba (all referenced with respect to the vacuum).

Figure 1. The current density (mA/cm^2) vs. applied voltage (V) and luminance (cd/m^2) vs. applied voltage (V) for devices made using blue-emitting PFO with and without the ETL.

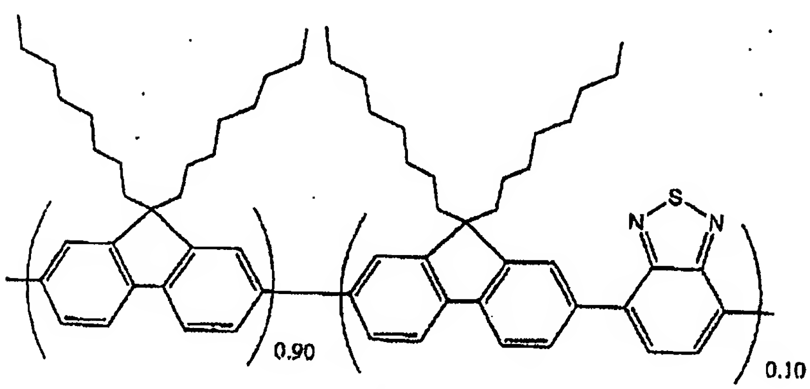
Figure 2. The luminous efficiency (cd/A) as a function of current density (mA/cm^2) for devices made with (a) PFO, (b) PFO-BT and (c) MEH-PPV with and without ETL. Insets: (a) Power efficiency (lm/W) vs. bias (V) for devices made by PFO with and without ETL; (b) and (c) brightness (cd/m^2) vs. current density (mA/cm^2) for devices made by PFO-BT and MEH-PPV with and without poly**1**.

Scheme 1. Synthesis of poly1 and poly4.

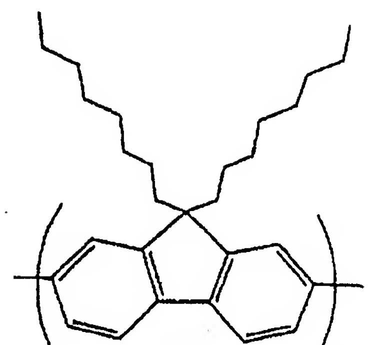


a = Toluene, water, $Pd(PPh_3)_4$, Na_2CO_3, 120 deg/48 hrs
b = THF, water, Iodomethane, RT/48 hrs

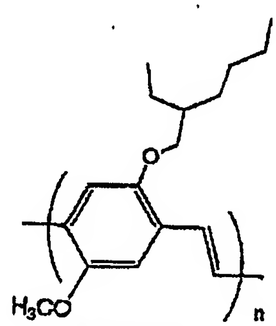
Scheme 2. Molecular Structures



PFO-BT



PFO



MEH-PPV

Scheme 3. Energy Levels

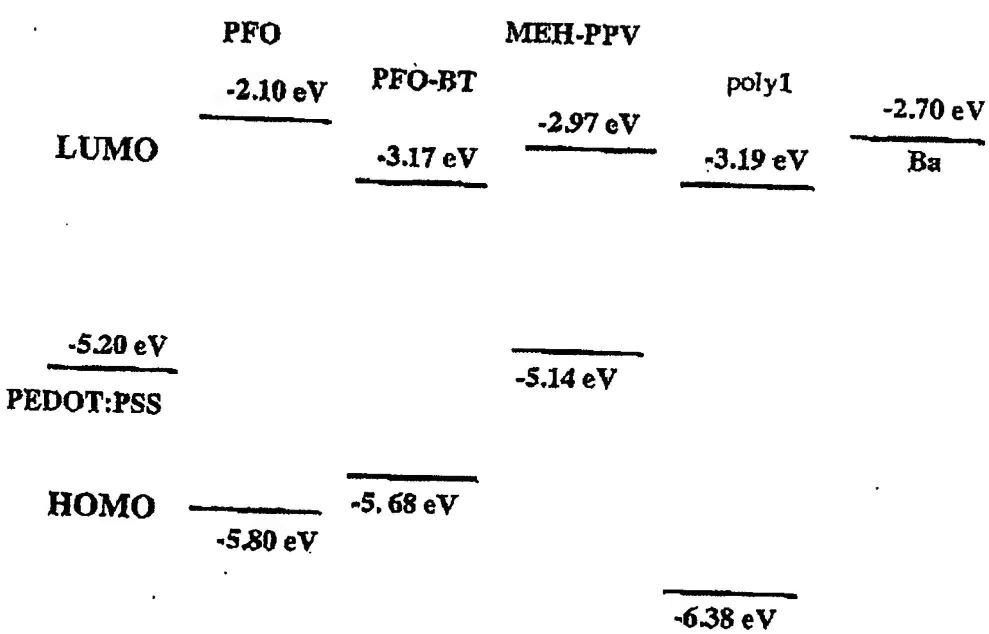
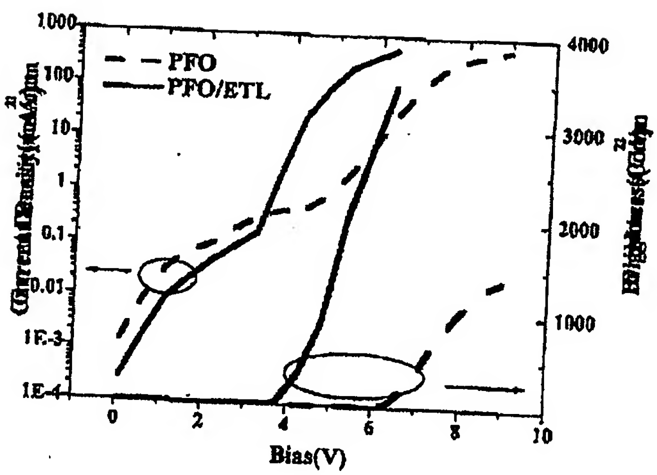
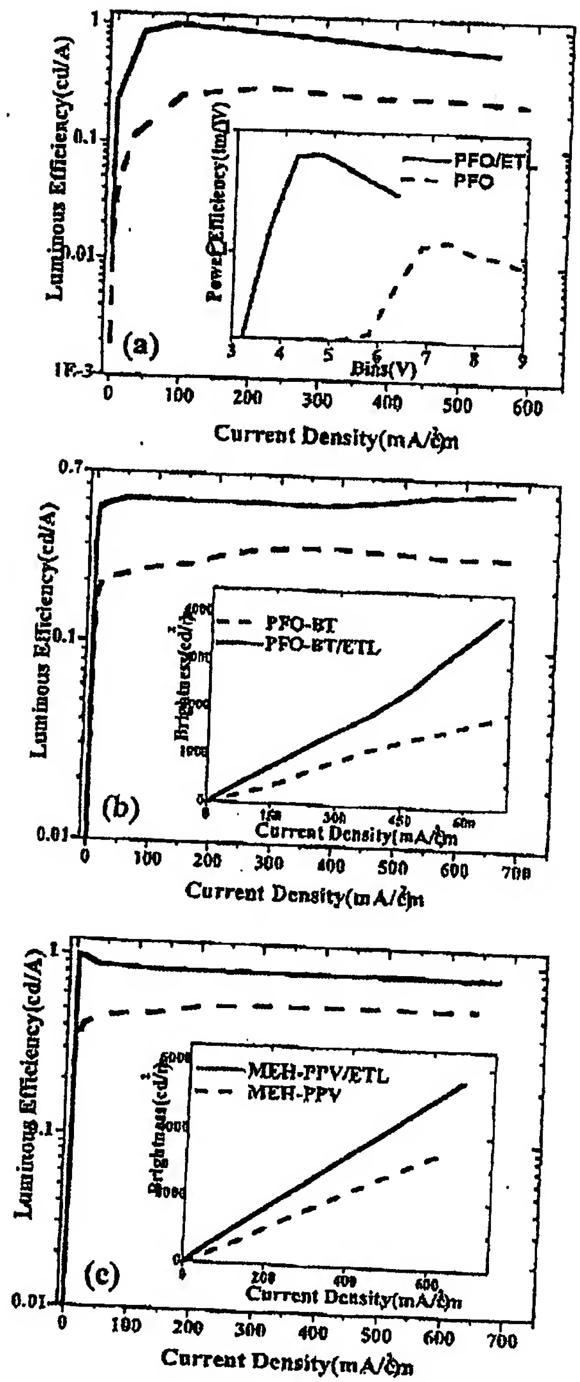


Figure 1



PFO
PFO/ETL
1000
100
10
1
0.1
0.01
1E-3
1E-4
4000
3000
2000
1000
0
2
4
6
8
10
Bias(V)

Figure 2



Luminous Efficiency(cd/A)
Power Efficiency(lm/W)
PFO/ETL
PFO
Bias(V)
(a)
Current Density(mA/cm²)
Luminous Efficiency(cd/A)
Brightness(cd/m²)
PFO-BT
PFO-BT/ETL
(b)
Current Density(mA/cm²)
Luminous Efficiency(cd/A)
Brightness(cd/m²)
MEH-PPV/ETL
MEH-PPV
(c)
Current Density(mA/cm²)